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ESTIMATION OF THE COLLISION-INDUCED DISSOCIATION RATES OF DIATOMIC AND TRIATOMIC MOLECULES

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FINAL REPORT ON
ANALYTICAL PHASE OF
Contract NAS 7-217

PREPARED FOR

Ames Research Center, NASA
Moffett Field, California

GM DEFENSE RESEARCH LABORATORIES

SANTA BARBARA, CALIFORNIA



AEROSPACE OPERATIONS DEPARTMENT



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Ames Research Center, NASA
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BY

C. Frederick Hansen

Feb. 1964

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FOREWORD

This work has been supported by the National Aeronautics and Space Administration under contract number NAS 7-217, entitled "Study of Dissociation and Ionization Rates Applicable to CO_2 - N_2 Mixtures." The present report is submitted as the final report on the analytical phase of the contract work.

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ABSTRACT

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Collision-induced dissociation rates for diatomic and triatomic molecules are estimated from a version of the available energy theory. The collision is assumed to excite one mode of internal momentum in an unbounded Boltzmann-like distribution, and the number of energy modes used in the dissociation process is taken to be the total number of internal modes of the molecule before dissociation less the number of internal modes in the molecular fractions produced. This model is found to agree with available experimental data, generally within a factor of 10, over a wide range of temperature and for a wide variety of collision partners.

AUTHOR

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INTRODUCTION

Quantitative knowledge of collision-induced reaction rates is required for the solution of a number of important aerospace problems. For example, Duff and Davidson^{(1)*} calculated the profiles behind normal shock waves in air, using experimental rate constants for O_2 , N_2 , and NO dissociation and the NO atom exchange reactions. Stimulated by the problems associated with space probes entering Venusian or Martian atmospheres, Howe, Viegas, and Sheaffer⁽²⁾ calculated similar profiles behind shock waves in CO_2 . In this case, the dissociation rate constants were not well known, with the exception of a value for $CO_2 + Ar$ collisions at $2700^\circ K$ determined by Brabbs, Belles, and Zlatarich.⁽³⁾ In order to bracket the range of uncertainty, Howe et al calculated parallel profiles in which the rate constants were varied about three orders of magnitude. One of the results observed from these calculations is that the profiles are not highly sensitive to the rate constants, and it appears that if these quantities could be estimated within a factor of 10, this might be sufficient for some engineering needs. Therefore, it is the purpose of this report to describe a method for estimating the collision-induced dissociation rates which, according to comparison with existing data, promises to predict these rates within one order of magnitude.

A number of rather different theoretical models have been proposed for rate processes. Glasstone, Laidler, and Eyring⁽⁴⁾ expound the activated complex

* Raised numbers in parentheses indicate references, listed at the end of this report.

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surface more rigorously, and particularly as the method is extended to triatomic molecules. So in spite of the strong aesthetic appeal of this method, which is quite rigorous in principle, there has not been great encouragement to develop this model further.

All of the above models were considered at various stages of the present investigation, but gradually it appeared that a version of the available energy theory described by Fowler and Guggenheim⁽¹¹⁾ might be most suitable for making the required order-of-magnitude estimates. This theory has often been held in disrepute because it does not predict the temperature dependence of the rate constants observed in some experiments. Nevertheless, it has been widely used as a convenient standard with which to compare experimental data,⁽¹²⁻¹⁷⁾ and it is the model used by Howe et al⁽²⁾ in their calculation of shock waves in CO₂. A very suggestive fact was the observation made by Palmer and Hornig⁽¹²⁾ four energy modes contributing to dissociation and a reasonable collision frequency fit the available energy theory to the experimental dissociation rate data for Br₂+A collisions, over a wide range of temperature. Following this lead, the present work takes up a sequence of investigations to examine a) if there is a logical reason why exactly four modes of energy should contribute to dissociation, b) if a similar choice might predict dissociation rates for a variety of other diatomic molecules and collision partners for which data were available, c) whether a logical extension of the model could be made to include the case of dissociation of triatomic molecules, and d) if the predictions for triatomic molecules would agree also with available experimental data.

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model, which seems to be appropriate for the case where complicated organic molecules are involved or where strong bonding forces exist between the collision partners. However, when one considers the implications of this model it does not seem so useful for diatomic and triatomic molecules dissociated by collision with inert particles, such as the noble gas atoms or molecules with closed shell electronic structures such as N_2 . Here, the interatomic potential forces are of short range and steep, and it is not clear how to define the "activated complex". Rather, a billiard-ball type of collision would seem to be a more realistic model in this case. A simple model for dissociation of diatomic molecules has been proposed by Rice,⁽⁵⁾ in which it is assumed that only the fraction of molecules with vibrational energy within kT of the dissociation limit are capable of being atomized by collision. Benson and Fueno⁽⁶⁾ have recently developed a version of this model for the recombination process which postulates that the collision deactivation occurs in a cascade sequence of single vibrational quantum jumps. Their results agree well with some experimental data; however, the model seems somewhat artificial in that it invokes the optical transition selection rule. Shuler et al find that, at high energies, the impulsive collisions of hard spheres with harmonic oscillators leads to strong transitions with multiple quantum jumps.^(7, 8) This would be expected, since the collision between rather massive nuclei with large momenta leads to very strong, inhomogeneous perturbations that are large compared to the quantum spacing. According to the correspondence principle, the classical model with a continuum of energy-states available should give a good approximation in such a case. Where classical mechanics is valid, perhaps the most straightforward approach is to calculate three body recombinations by counting the flux of reacting systems across a given surface in phase space. Wigner⁽⁹⁾ shows that if such a surface, separating the dissociated from the bound state, is properly chosen - namely so the flux across the surface is a minimum - then the recombination rate is rigorously determined. Keck⁽¹⁰⁾ has recently improved Wigner's calculations by using variational methods to find minimum values for surfaces having plausible functional forms. However, it is clear that the calculations must become increasingly intricate as one attempts to define this

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DISSOCIATION-RATE MODEL

For the collision-induced dissociation



The rate coefficient α is defined by

$$\frac{d}{dt} [AB] = -\alpha [A] [B] \quad (2)$$

where the brackets denote concentrations. The coefficient α may be expressed as the product of a collision rate θ and the probability P , that dissociation results from a single collision

$$\alpha = \frac{\theta P}{s} \quad (3)$$

The symmetry number s is unity, unless the molecules AB and M are identical, in which case it must equal 2 to avoid counting systems twice in Equation (2).

For a gas with an equilibrium distribution, θ is given by

$$\theta = (2\pi\mu kT)^{-3/2} \int_0^{\infty} \frac{p}{\mu} S(p) \exp\left(\frac{-p^2}{2\mu kT}\right) 4\pi p^2 dp \quad (4)$$

where p is the momentum of the colliding particles in center of mass coordinates, μ is the reduced mass, and $S(p)$ is the collision cross section for both favorable and unfavorable events.

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The cross-section function is not precisely known, but it is not difficult to estimate within a factor of about two, sufficient for the present purposes. To a first approximation, the wave functions of outer electrons extend about the same range for all atoms and only slightly more for diatomic molecules, such that all cross sections are the order of $30 \times 10^{-16} \text{ cm}^2$. Perhaps a somewhat better approximation is obtained if a momentum cross section is used. In this case, the cross section decreases with increasing momentum and it will be assumed here that S has the form

$$S = S_{\infty} \left(1 + \frac{8kC\mu}{\pi p^2} \right) \quad (5)$$

which is equivalent to the Sutherland cross section used for viscosity. Sutherland's constant C is of the order of a few hundred degrees K for most atoms and molecules. With a cross section given by Equation (5), the collision rate becomes

$$\theta = \left(\frac{8kT}{\pi \mu} \right)^{1/2} S_{\infty} \left(1 + \frac{4C}{\pi T} \right) \quad (6)$$

The crucial problem is to evaluate the probability factor P in Equation (3). Fowler and Guggenheim⁽¹¹⁾ calculate P by counting the fraction of systems which flow across a surface in phase space with energy in n modes exceeding the dissociation energy. They took the viewpoint that one of these n modes is the kinetic energy of the colliding molecules along the coordinate between centers at impact, and that the reaction surface is normal to this coordinate. However, the equations which they derive are valid for the crossing of any surface normal to one of the generalized coordinates, either before or after collision, provided the density in phase space is distributed according to a Boltzmann function involving only classical terms in squared momenta or coordinates. This is a reasonably good approximation for the molecules in a dilute gas prior to collision, so it is quite appropriate for the Fowler-Guggenheim model. Only the number of modes which should contribute to dissociation is uncertain.

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In the following report, the viewpoint will be taken that the probability of dissociation by collision is the fraction of the flux crossing a given surface in phase space after collision, in which the energy in internal modes of the molecule AB is sufficient to lead to dissociation. This clarifies the problem of selecting the number n , but it is not as evident what the phase density should be. It is argued that where the collision partners are inert and the gas is in equilibrium, the density after collision is still approximately a classical Boltzmann-like distribution. To the order of this approximation, the calculation of the factor P becomes relatively simple.

The general expression for the number of phase points crossing a surface per unit time is

$$F = \int \rho \frac{dS/dt}{\text{grad } S} d\sigma \quad (7)$$

where the surface S is defined by a function of the generalized coordinates q_k and their conjugate momenta p_k ,

$$S(p_k, q_k) = \text{constant} \quad (8)$$

ρ is the density of points in phase space, and $d\sigma$ is the surface element. The concept "surface" means here a $2m - 1$ dimensional subspace, where m is the total number of position or momentum type coordinates in the phase space considered. According to Newtonian mechanics, the derivative dS/dt is the Poisson bracket

$$\frac{dS}{dt} = \left\{ S, H \right\} = \sum_{k=1}^m \left(\frac{\partial H}{\partial p_k} \frac{\partial S}{\partial q_k} - \frac{\partial H}{\partial q_k} \frac{\partial S}{\partial p_k} \right) \quad (9)$$

where H is the Hamiltonian, or the total energy expressed in terms of the generalized coordinates and momenta. Normally, the Hamiltonian involves only momenta squared terms plus a potential which is some function of the coordinates

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$$H = \sum_{k=1}^m \frac{p_k^2}{2\mu_k} + V(q_k, \dots) \quad (10)$$

The constants μ_k are either a reduced mass or a moment of inertia. In subsequent analysis, the reaction crossing surfaces will be taken as surfaces orthogonal to the coordinate q_k that is conjugate to a collision-excited momentum p_k . Then

$$S = q_k = \text{constant} \quad (11a)$$

$$\text{grad } S = 1 \quad (11b)$$

Then when the Hamiltonian is given by Equation (10), the Poisson bracket is just p_k/μ_k , and the flux across this surface is

$$F = \int \frac{p_k}{\mu_k} \rho \, d\sigma \quad (12)$$

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DISSOCIATION OF DIATOMIC MOLECULES

The final objective of this study is to develop a method for estimating the dissociation rates of triatomic molecules. However, some features of the model used can be conveniently explained in terms of diatomic molecules, and there now exists a body of experimental data for these molecules⁽¹²⁻¹⁷⁾ that can provide a valuable check on the order of approximation involved. Therefore, the dissociation of diatomic molecules will be treated here first.

The collision partner M is supposed to be extremely inert with respect to the molecule AB . By this, it is meant that the interaction potentials are very short range, very steep, and repulsive. Then the molecule M will normally interact with just one of the atoms of the diatomic molecule, either A or B , along potentials that have approximate spherical symmetry. Under this condition, momentum exchange occurs only along the coordinate between centers at the moment of closest approach. The collision process may therefore be approximated by a sudden discontinuity in one of the internal momentum coordinates of the molecule AB , without change in the other two momentum coordinates (which are orthogonal to the excited momentum) or in the inter-atomic distance coordinate.

The coordinates of molecule AB that are not affected by collision have a Boltzmann distribution by definition, and these distributions are bounded by the requirement that the molecule is stable before collision. The excited momentum coordinate must also have a Boltzmann-like distribution if the gas is defined to be in equilibrium, for the excited molecules that are stable become a part of the equilibrium distribution. However, in this case the distribution may be unbounded and independent of the energy residing in the other internal modes, since the molecule is not obliged to be stable after the collision event. It seems

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plausible to assume that the Boltzmann-like distribution extends to the unstable excited molecules as well as to those of lower energy. This is similar to the concept that a collision complex, in the Eyring theory, should have a Boltzmann distribution at the gas temperature, T .

The number of modes n which contribute to dissociation of the excited diatomic molecule is unambiguous. The molecule must dissociate when the total energy in the four internal modes (two rotational momentum modes, one vibrational momentum mode, and one vibrational potential mode) exceeds the dissociation energy plus the energy of a small rotational barrier. All other coordinates associated with the molecule AB or with the particle M are irrelevant to the problem once the collision has occurred, provided the particle M is sufficiently inert. Thus the state of AB , as far as dissociation is concerned, is described by a point moving in a 4-dimensional phase space. The reaction surface will be taken as the 3-dimensional subspace across which the flux suffers a maximum discontinuity — that is, the surface normal to the excited momentum coordinate. This is not the only possible choice for S , but at least it makes the integrations easy to accomplish. The excited momentum coordinate will be designated by p_1 , the two residual momenta by p_2 and p_3 , and the difference $r - r_0$ by q , where r is the interatomic distance between A and B , and r_0 is the equilibrium value of r . Then, if the Boltzmann density distribution for a classical, rotating harmonic oscillator is used, the element of flux across the surface S is proportional to (see Equation 12)

$$dF \propto \exp \left\{ -\frac{p_1^2 + p_2^2 + p_3^2}{2\mu k T} - \frac{2\pi^2 \mu \omega^2 q^2}{k T} \right\} p_1 dp_1 dp_2 dp_3 dq \quad (13)$$

where ω is the vibrational frequency and μ is now the reduced mass of the diatomic molecule. Transform to the energy coordinates

$$\eta = \frac{p_1^2}{2\mu} \quad (14a)$$

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$$d\eta \propto p_1 dp_1 \quad (14b)$$

$$\epsilon = \frac{p_2^2 + p_3^2}{2\mu} + 2\pi^2 \mu \omega^2 q^2 \quad (15a)$$

$$\epsilon^{1/2} d\epsilon \propto dp_2 dp_3 dq \quad (15b)$$

Then the fraction of the flux crossing S with energy in the excited mode between η and $\eta + d\eta$, and the residual energy in the remaining three modes between ϵ and $\epsilon + d\epsilon$, is given by

$$dP = \frac{e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon}{\Gamma(3/2) (kT)^{3/2}} \frac{e^{-\eta/kT} d\eta}{kT} \quad (16)$$

The denominators in Equation (16) are just the normalization constants required so that the integral over all possible energies yields a total fraction, or probability, of unity. Actually the energy ϵ is bounded by the dissociation energy D (neglecting the effect of the rotational barrier⁽¹⁰⁾ and the energy initially in the excited mode before collision), whereas the normalization constant $\Gamma(3/2) (kT)^{3/2}$ is for an unbounded Boltzmann distribution. However, for the temperatures of interest, the ratio D/kT is generally appreciably greater than unity, in which case the correction required is small. It will be neglected here for simplicity.

Integrating Equation (16) over all combinations of internal energy greater than D , with η unbounded but with the restriction $\epsilon \leq D$, one obtains

$$P = \int_0^D \frac{e^{-\epsilon/kT} \epsilon^{1/2}}{\Gamma(3/2) (kT)^{3/2}} \left[\int_{D-\epsilon}^{\infty} \frac{e^{-\eta/kT} d\eta}{kT} \right] d\epsilon \quad (17a)$$

$$P = \frac{4}{3\pi^{1/2}} \left(\frac{D}{kT} \right)^{3/2} e^{-D/kT} \quad (17b)$$

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Several refinements to the above model can be added in an approximate manner without great complication. One of these is due to the effect of the rotational barrier discussed by Keck⁽¹⁰⁾. The rotation of the diatomic molecule contributes a term $\ell^2/2\mu r$ to the effective interatomic potential. This creates a maximum in the potential which is a function of the angular momentum quantum number ℓ . Thus, instead of integrating over a domain bounded by a simple spherical surface of constant energy (as in Equation 17a), the domain should be bounded by an ellipsoidal-like surface in phase space. Such an integration is difficult to perform, but an idea of the magnitude of the correction can be obtained by averaging $\ell^2/2\mu r$ over both components of the angular momentum (note that the diatomic molecule has two rotational momentum modes so that $\ell^2 = \ell_1^2 + \ell_2^2$). The result is kT . Thus on the average the maximum in the effective potential is about $D + kT$, and the lower limit of the inner integral in Equation (17a) can be replaced by $D + kT - \epsilon$. The upper limit of the outer integral in Equation (17a) should also be increased by kT , according to the same argument. However, the value of ϵ is limited to $D + kT$ less the energy initially residing in the mode excited by collision. On the average this is $kT/2$, and to the order of accuracy considered it is then consistent to take the upper limit of the outer integral as $D + kT - kT/2$. With these changes, Equation (17) becomes

$$P = \int_0^{D+kT/2} \frac{e^{-\epsilon/kT} \epsilon^{1/2}}{\Gamma(3/2) (kT)^{3/2}} \left[\int_{D+kT-\epsilon}^{\infty} \frac{e^{-\eta/kT} d\eta}{kT} \right] d\epsilon \quad (18a)$$

$$P = \frac{4}{3\pi^{1/2}} \left(\frac{D}{kT} + \frac{1}{2} \right)^{3/2} e^{-(D/kT + 1)} \quad (18b)$$

and Equation (18b) will be used for the comparisons with measured diatomic molecule dissociation rates which follow.

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Other corrections could be considered. For example, at low temperatures the integrations over vibrational states should be replaced by quantum summations. In the denominator of Equation (18a), one of the factors kT is just the vibrational partition function and can be replaced by the quantum partition function, $hw/(1 - e^{-hw/kT})$. However, the quantum summation is not so easy to introduce into the numerator. Fortunately, the correction is not highly important until D/kT is greater than $10D/hw$, normally outside the temperature range of interest. At these low temperatures, the gas may often be considered frozen in the associated state, at least for aerodynamic purposes. Only in the case of H_2 is the ratio D/hw unusually small (because of the low atomic weight and the stiff bond involved) so that the effect seems noticeable at temperatures of interest. In this case, it will be seen later, the substitution of the quantum partition function in the denominator appears to bring about satisfactory agreement between theory and data. At high temperatures, one might expect anharmonic effects to become important. Again such corrections complicate the analysis to the point where a rigorous approach, such as developed by Wigner⁽⁹⁾ and Keck,⁽¹⁰⁾ might as easily be followed. For the present, it will be of interest to inquire as to how well Equation (18) will correlate with experimental data, without further modification.

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CALCULATIONS OF DIATOMIC MOLECULE DISSOCIATION RATES

The theoretical dissociation rate for diatomic molecules given by Equations (3), (6), and (18) is

$$\alpha = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \frac{S_{\infty}}{s} \left(1 + \frac{4C}{\pi T} \right) \frac{4}{3\pi} {}^{1/2} \left(\frac{D}{kT} + \frac{1}{2} \right)^{3/2} e^{-\left(\frac{D}{kT} + 1 \right)} \quad (19)$$

In order to compare the theoretical model with experiment, Equation (19) has been used to calculate dissociation rates for Cl_2 , Br_2 , I_2 , N_2 , O_2 , and NO with a variety of collision partners, from noble gases and other atoms to diatomic molecules. The ratios D/k and the collision cross-section parameters used in these calculations are listed in Table I. For collisions between unlike molecules (denoted by subscripts 1 and 2) it has been assumed that the cross-section parameters are given by

$$S_{\infty} = \left(\frac{\sqrt{S_{1\infty}} + \sqrt{S_{2\infty}}}{2} \right)^2 \quad (20)$$

$$C = \frac{C_1 + C_2}{2} \quad (21)$$

Some of the experimental data are expressed as recombination rates, k_r , for the reverse three-body collision defined by Equation (1). These data were transformed to a dissociation rate, k_d , by the relation

$$k_d = k_r K_c \quad (22)$$

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where K_c is the equilibrium constant in units of standard concentration. The equations used to compute the values of K_c required are listed in Table II. Rice⁽¹⁸⁾ discusses some of the questions concerning the validity of this procedure and concludes that, even if the gas is not strictly in equilibrium, the ratio of the observable rates should still be the equilibrium constant. Therefore, the dissociation rate calculated from Equation (22) is presumed to be the rate that would have been measured in that experiment.

Experimental values of the dissociation rates and recombination rates are now available for a number of different diatomic molecules. Comparisons of these theoretical and experimental rates are shown in Figures 1 through 4, where the logarithm of the ratio α/k_d is graphed as a function of the dimensionless temperature kT/D . Figure 1 shows results for the dissociation of the halogens, Figure 2 for the dissociation of O_2 , Figure 3 for the dissociation of N_2 and NO , and Figure 4 for the dissociation of H_2 and D_2 .

A number of individual data points are shown in Figure 1 for $Br_2 + A$ and the $Br_2 + Br_2$ collisions measured by Palmer and Hornig.⁽¹²⁾ These give a representative picture of the type and magnitude of the scatter that can be expected from a carefully conducted set of experiments. The remaining data points on Figures 1-4 often represent the average of a group of individual data points with similar or greater scatter. Sources of the additional data for the halogens are Strong, Chien, Graf, and Willard⁽¹⁹⁾ (low temperature Br_2 and I_2 data), Britton, Davidson, Gehman, and Schott⁽²⁰⁾ (high-temperature I_2 data) and Hiraoka and Hardwick⁽¹⁷⁾ (Cl_2 data). The solid curve on Figure 1 represents the formula fit by least mean squares to the data of Palmer and Hornig⁽¹²⁾ and of Strong, Chien, Graf and Willard.⁽¹⁹⁾ The dashed curve is the extrapolation of this formula outside the range of data.

Sources of the data shown on Figure 2 for O_2 dissociation are Mathews,⁽¹³⁾ Byron,⁽¹⁴⁾ Camac and Vaughan,⁽¹⁵⁾ Rink, Knight, and Duff,⁽²¹⁾ Marshall⁽²²⁾ Schexnayder and Evans,⁽²³⁾ Wray,⁽²⁴⁾ and Anderson.⁽²⁵⁾ Several empirical formulae fitting the data on dissociation of air molecules are collected in a valuable summary paper by Wray.⁽²⁶⁾

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For Figure 3, the N_2 dissociation rate data at high temperature is primarily due to Byron,⁽¹⁴⁾ with a few additional points from Allen, Keck, and Camm.⁽²⁷⁾ Low-temperature N_2 data is from Herron and Franklin,⁽²⁸⁾ Harteck, Reeves, and Manella,⁽²⁹⁾ and Marshall.⁽²²⁾ High-temperature data for NO dissociation is taken from Freedman and Daiber⁽¹⁶⁾ and Wray and Teare.⁽³⁰⁾

The H_2 dissociation rate data exhibits somewhat more scatter and wider deviation from the simple available energy model than does the data for the heavier molecules. This is not unexpected, since the classical model should not work well for vibrational transitions of these light particles, and the theory of Benson and Fueno⁽⁶⁾ would perhaps be more appropriate in this case. Nevertheless, the H_2 and D_2 dissociation-rate data still generally lie within a factor of 20 of the values predicted with Equation (18), and if one of the factors kT in the denominator is replaced by the quantum vibrational partition function, the result is improved to a factor of ten, as shown on Figure 4. (It should be noted that this does not constitute a sufficient account of quantum effects, and the improvement may be fortuitous.) The H_2 rate data shown on Figure 4 came from Rink,⁽³¹⁾ Patch,⁽³²⁾ Sutton,⁽³³⁾ and Marshall.⁽²²⁾ A number of additional data points for H_2 due to Pitchard, Duff, Amdur, Steiner, Senftleben, and Gardiner are summarized in graphical form in a paper by Bauer.⁽³⁴⁾ A single, early, low-temperature measurement by Smallwood has been excluded because it seems much too low to be consistent with the other measurements. The D_2 dissociation-rate data shown on Figure 4 are from Sutton.⁽³³⁾

The above is not necessarily a complete list of presently available experiments on diatomic dissociation rates, but it seems extensive enough to provide a reasonable check on the theoretical expression, Equation (19).



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DISCUSSION OF RESULTS FOR DIATOMIC MOLECULES

It can be seen from Figures 1 through 4 that the experimental data generally agree with the values predicted within a factor of 10. In view of the rather approximate nature of the collision cross sections and other assumptions, this agreement is very satisfactory. The discrepancies between theory and experiment are not much greater than scatter in the data or the deviations between various investigators.

In general, collisions with inert partners such as the noble gases give dissociation rates lower than predicted by a factor of about 5. On the other hand, collisions with atoms having unpaired electrons give dissociation rates larger than predicted by a factor of about 3, while diatomic molecule collision partners give about the same dissociation rate as predicted. The electrons in such molecules are generally paired in ground-state molecular orbits, so the molecules behave much more like inert collision partners than the atoms, though not to the same extent as the noble gases. The above factors can be used as empirical corrections to force closer agreement between experiment and the theoretical model. These corrections could be considered as modest adjustments of the collision cross sections.

The approximate agreement between theory and experiment extends to a variety of collision partners with different dissociation energies and at widely different temperatures. It seems reasonable to expect that the theory might be equally successful in predicting rates for dissociation of other diatomic molecules for which data are lacking. It may be pointed out that rates deduced from recombination measurements appear to fit the theory as well as direct dissociation rate data. This tends to support Rice's contention⁽¹⁸⁾ that the ratio of the observed rates should be the theoretical equilibrium constant as given in Equation (22).

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It remains to reconcile the statement frequently made that the available energy theory does not agree with experimental observations. What is usually meant by this statement is that a set of data, taken over a narrow temperature interval, has been fit by a least-mean-squares method to a formula derived by Fowler and Guggenheim

$$\alpha = \frac{\theta}{\Gamma\left(\frac{n+1}{2}\right)} \left(\frac{D}{kT}\right)^{\frac{n-1}{2}} e^{-D/kT} \quad (23)$$

where n is the number of classical energy modes in which the dissociation energy is stored, and θ is the collision rate, assumed to vary about as $T^{1/2}$. It is often found that the empirical value for n corresponds to an impossibly large number of modes and that the value for θ is unreasonable in view of known magnitudes for the cross sections. However, these empirical coefficients depend on derivatives of the data with respect to temperature, and, in view of the typical dispersion in the data obtained, these derivatives can hardly be taken seriously when the data covers only a narrow range in temperature. Whenever these least-squared derivatives are anchored by additional data taken at widely different temperatures, the coefficients correspond to a reasonable collision rate and a value of n close to 4. This was first observed by Palmer and Hornig⁽¹²⁾ for the case of Br_2 dissociation, and the comparison shown on Figures 1 - 4 indicate that this will be the case for other diatomic molecules as well. Treanor and Marrone⁽³⁵⁾ have analyzed the coupling between vibrational relaxation and dissociation rates. They find that dissociation depopulates the upper vibrational states behind strong shock waves, such that the observed dissociation rate is less than the equilibrium rate that would occur if the vibrational states were fully excited. This could explain why data taken in shock tubes often indicates a different temperature dependence of the pre-exponential factor than predicted for the equilibrium model. In view of the above, only the absolute values of the dissociation rate data are used for comparisons with theory, and the experimental temperature derivatives are considered suspect.

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It is concluded that the comparisons between theory and experiment shown on Figures 1 - 4 establish a necessary condition, though not a sufficient condition, that is favorable to the available energy model, as far as diatomic molecule dissociations are concerned. The next section will consider the problem of treating triatomic molecules with a similar model.

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DISSOCIATION OF TRIATOMIC MOLECULES

Where polyatomic molecules are concerned, the number of energy modes which contribute to dissociation will be taken as the number of internal modes which disappear when the molecule breaks up into two fractions. The remaining internal modes are presumed to be fully excited in a Boltzmann distribution at the gas temperature T , since the molecular fractions formed are by definition a part of the equilibrium background gas. Thus a linear triatomic molecule, such as CO_2 , has 10 modes of internal energy (two rotational modes, one symmetric stretching vibration, one asymmetric stretching vibration, two bending vibrational modes, and one potential mode associated with each of the four vibrational momentum modes). If this molecule dissociates into an atom and a diatomic fraction with four modes of internal energy, then n is taken to be six. A nonlinear triatomic molecule, such as NO_2 , has 9 modes of internal energy (one additional rotational mode, but one less bending vibrational mode with its accompanying potential mode, when compared with the linear triatomic molecule), and for the same dissociation products, n is taken to be five.

Assume that again the collision excites but one mode of internal energy, that two rotational modes increase the effective potential along any stretching coordinate by the amount kT , and that the $(n-1)$ unexcited modes are bounded by $D + kT/2$, as before. Then the probability factor becomes

$$P = \frac{\int_0^{D + \frac{kT}{2}} \epsilon^{\frac{(n-3)}{2}} \exp(-\epsilon/kT) \left[\int_{D + kT - \epsilon}^{\infty} \exp(-\eta/kT) d\eta \right] d\epsilon}{\Gamma\left(\frac{n-1}{2}\right) (kT)^{\frac{n+1}{2}}} \quad (24)$$

$$P = \frac{\left(\frac{D}{kT} + \frac{1}{2}\right)^{\frac{n-1}{2}} e^{-\left(\frac{D}{kT} + 1\right)}}{\Gamma\left(\frac{n+1}{2}\right)} \quad (25)$$

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Equation (25) will be used for making a comparison with experimental dissociation rates for triatomic molecules in the following section. First, however, it is important to show that if the collision excites more than one energy mode, the result given by Equation (25) is not greatly altered.

In the case of triatomic molecules, it is conceivable that the collisions should excite at least two modes of internal energy. For example, an end-on collision with the linear CO_2 molecule could be expected to excite both the symmetrical and the asymmetrical vibrational momentum modes. Similarly, a collision normal to the molecular axis could be expected to simultaneously excite one of the bending vibrational modes and one of the rotational modes. When two excited modes are allowed, the integrations become somewhat more involved

$$P = \int_0^D \frac{\epsilon^{\frac{n-4}{2}} e^{-\epsilon/kT}}{\Gamma\left(\frac{n-2}{2}\right) (kT)^{(n-2)/2}} \left[\int_{D-\epsilon}^{\infty} \frac{\eta^{1/2} e^{-\eta/kT} d\eta}{\Gamma(3/2) (kT)^{3/2}} \right] d\epsilon \quad (26)$$

where for simplicity the corrections for the rotational barrier and for the initial energy in the excited mode have been overlooked. Upon integrating the inner integral by parts, one may express Equation (26) as

$$P = P_0 + P_1 \quad (27)$$

where

$$P_0 = \frac{e^{-D/kT}}{\Gamma\left(\frac{n-2}{2}\right) \Gamma\left(\frac{3}{2}\right)} \int_0^{D/kT} x^{\frac{n-4}{2}} \left(\frac{D}{kT} - x\right)^{1/2} dx \quad (28a)$$

$$P_1 = \frac{\pi}{2\Gamma\left(\frac{n-2}{2}\right) \Gamma\left(\frac{3}{2}\right)} \int_0^{D/kT} x^{\frac{n-4}{2}} e^{-x} \left\{ 1 - \operatorname{erf}\left(\frac{D}{kT} - x\right)^{1/2} \right\} dx \quad (28b)$$

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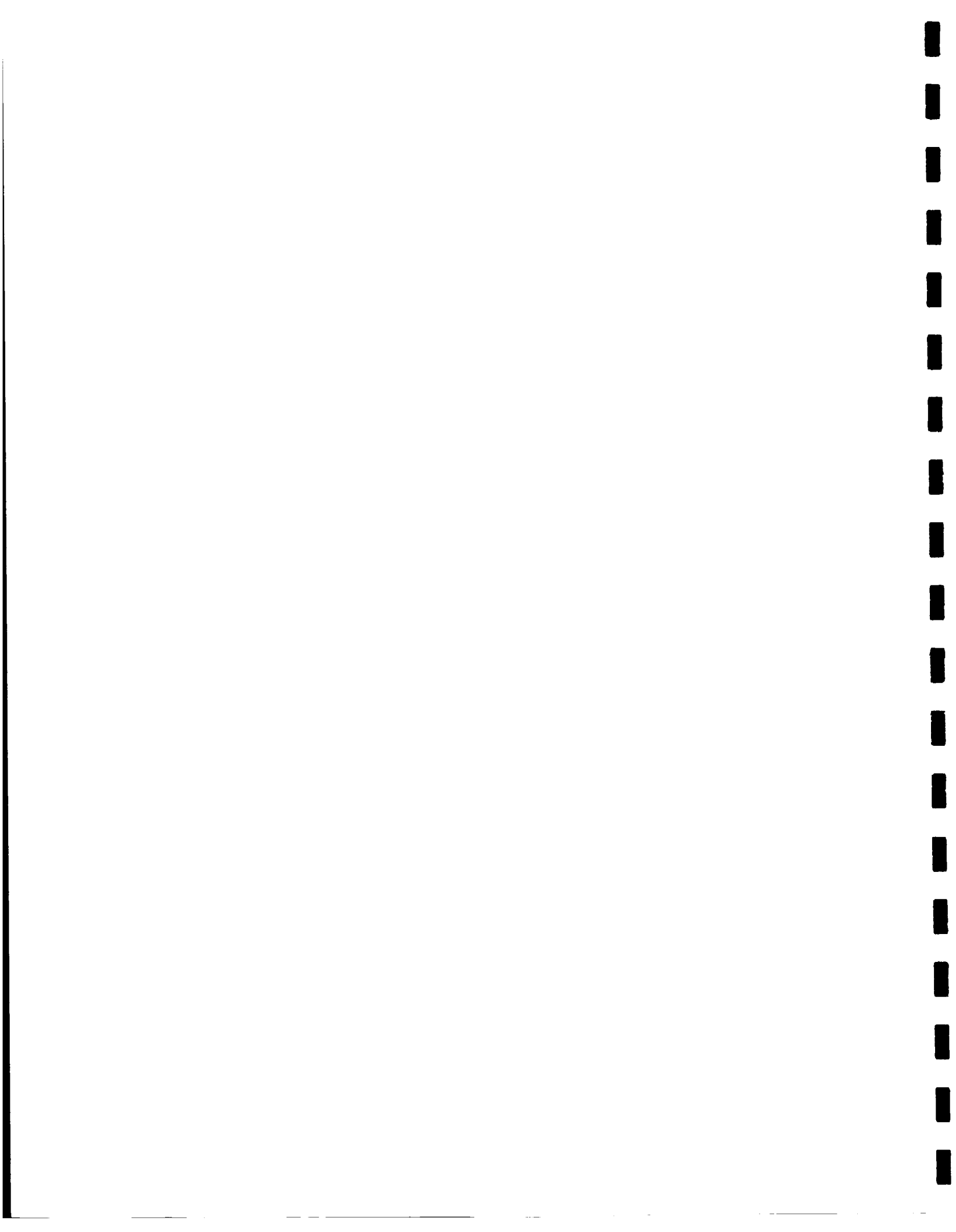
For $n = 5$ or 6 , the leading term P_0 reduces to the same result as Equation (25), where only one mode of internal momentum is assumed to be excited. Thus P_1 represents the correction to this result required when a second mode is excited. It can be seen that P_1 will be small compared to P_0 whenever D/kT is large compared to unity, as the factor $\{1 - \text{erf}(D/kT - x)^{1/2}\}$ is sizable only where x is $(D/kT - 1)$ or larger. If the integral in Equation (28b) is integrated from $(D/kT - 1)$ to D/kT , the result is approximately the value of the integrand at D/kT . Then P_1 is approximately given by

$$P_1 \approx \frac{\pi}{2\Gamma\left(\frac{n-2}{2}\right)\Gamma\left(\frac{3}{2}\right)} \left(\frac{D}{kT}\right)^{\frac{n-4}{2}} e^{-D/kT} \quad (29)$$

From Equation (25) it can be seen that the ratio P_1/P_0 is approximately

$$\frac{P_1}{P_0} \approx \frac{\pi}{2} \frac{\Gamma\left(\frac{n+1}{2}\right)}{\Gamma\left(\frac{n-2}{2}\right)\Gamma\left(\frac{3}{2}\right)} \left(\frac{D}{kT}\right)^{-3/2} \quad (30)$$

which is small for large values of (D/kT) . Thus the influence of 2-mode excitation by collision is considered to be a small correction on the result for single-mode excitation at the temperatures of interest.



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CALCULATION OF TRIATOMIC MOLECULE DISSOCIATION RATES

Dissociation rates for the triatomic molecules have been calculated from Equation (3) using the probability factor given by Equation (25). Experimental data for the triatomic molecules is rather meager compared to the diatomic molecule, but the comparisons with available data are shown in Figure 5. The H_2O vapor point is an estimate by Duff⁽³⁶⁾ and the NO_2 rates are from Ford and Endow⁽³⁷⁾ and Huffman and Davidson.⁽³⁸⁾ Similar rates are quoted by Bortner and Golden⁽³⁹⁾ and Nawrocki and Papa.⁽⁴⁰⁾ The O_3 rate is also from Bortner and Golden⁽³⁹⁾ and is about the same as the rate deduced from a recombination rate published by Benson.⁽⁴¹⁾ The low-temperature point for CO_2 dissociation by A collisions is a group of measurements due to Brabbs, Belles, and Zlatarich⁽³⁾ centered around 2700°K . The two connected points at higher temperature cover data obtained by Davies⁽⁴²⁾ between 4000° and 6000°K , and the remaining points are measurements made by Steinberg⁽⁴³⁾ at GM Defense Research Laboratories. In general, these results for the triatomic molecules agree with the predicted values within the stated margins. The one exception is the high-temperature CO_2 data by Davies which is about a factor of 30 lower than predicted at 6000°K , though below 5000°K the agreement is again within a factor of 10. Steinberg's measured rates are about a factor of three higher than Davies' around 6000°K , and although this is not a significant difference in view of the scatter in both sets of data, the higher rates of Steinberg do generally agree with the theory within a factor of 10. In fact, the CO_2 dissociation rates with A collision partners follow the same pattern as do the diatomic molecules with A collision partners; namely, the predicted values are about a factor of 5 to 10 higher than measured when viscous cross sections are used. Possibly the vibrational population depletion produced behind strong shock waves might again explain the deviation in some of the higher temperature data. At any rate, considering

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the uncertainties and scatter in data, the comparisons shown on Figure 5 are judged sufficiently favorable to justify use of the available energy model for triatomic molecule dissociations, at least for the present degree of approximation.

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CONCLUDING REMARKS

The results of Palmer and Hornig⁽¹²⁾ suggested that the available energy theory of dissociation rates could agree with experiment over wide temperature limits, if four degrees of freedom were chosen to contribute to dissociation and if collision cross sections the order of molecular size were assumed. In the present paper, it is argued that the molecules can be categorized as stable or unstable as they cross a surface in phase space after the collision event; further, if the gas is in equilibrium and the collision partners are inert, the flux across this surface should result from a Boltzmann-like density distribution. In the case of diatomic molecules, the molecule dissociates when the energy in the four available internal-energy modes exceeds the dissociation limit. In the case of polyatomic molecules, the number of internal-energy modes used in the dissociation process is taken to be the total number of internal-energy modes available in the polyatomic molecule less the total number of internal modes in the molecular fractions produced by the dissociation. The collision is assumed to excite one mode of internal energy in an unbounded Boltzmann-like distribution. It is found that only small corrections are required if the collision should excite two modes of internal energy in the case of triatomic molecules. This model is found to agree with available experimental data, generally within a factor of 10, over a wide range of temperature and for a wide variety of collision partners, covering dissociation of both diatomic and triatomic molecules.

The model described above is inherently a simple, order-of-magnitude model. If one attempts to add refinements, the integrations required rapidly become more complicated and a more rigorous procedure, such as that developed by Wigner⁽⁹⁾ and Keck,⁽¹⁰⁾ might as easily be followed. In any field of research

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with a long history seeking to develop theoretical models, such as the field of reaction kinetics, there is certain to be resistance to the idea that any simple model could possibly explain such complex processes. Nevertheless, the results suggest that the available energy model may have an element of reality. Even if this were not the case, the results still constitute an empirical correlation method of value in many engineering applications.

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TABLE I. CROSS SECTION PARAMETERS

<u>Molecule</u>	<u>S_{∞}</u>	<u>C</u>	<u>D/k</u>
Cl_2	$44.0 \times 10^{-16} \text{ cm}^2$	330°K	$28,730^\circ\text{K}$
Br_2	42.7	533	22,860
I_2	58.3	568	17,880
H_2	18.3	84	51,960
D_2	18.3	84	52,860
N_2	33.0	104	113,200
O_2	29.2	125	58,900
NO	29.6	128	75,240
CO_2	27.2	213	63,290
He	11.8	80	
Ne	17.7	56	
A	28.0	142	
Kr	32.5	188	
Xe	39.7	252	
H	13.5	703	
D	13.5	703	
N	16.5	1312	
O	12.5	649	

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TABLE II. EQUILIBRIUM CONSTANTS ($d = D/kT$)

Reaction	$\ln K_c$ (in molecules/cm ³)
$\text{Br}_2 \rightleftharpoons 2\text{Br}$	$\ln K_c = -d - \frac{1}{2} \ln d + 57.854 + \ln(1 - e^{-.02032d})$ $+ 2 \ln(1 + \frac{1}{2} e^{-.2317d})$
$\text{I}_2 \rightleftharpoons 2\text{I}$	$\ln K_c = -d - \frac{1}{2} \ln d + 57.653 + \ln(1 - e^{-.01725d})$ $+ 2 \ln(1 + \frac{1}{2} e^{-.6106d})$
$\text{O}_2 \rightleftharpoons 2\text{O}$	$\ln K_c = -d - \frac{1}{2} \ln d + 58.839 + \ln(1 - e^{-.03856d})$ $+ 2 \ln(1 + \frac{3}{5} e^{-.003866d} + \frac{1}{5} e^{-.005526d})$ $- \ln(1 + \frac{2}{3} e^{-.1931d} + \frac{2}{3} e^{-.3220d})$
$\text{N}_2 \rightleftharpoons 2\text{N}$	$\ln K_c = -d - \frac{1}{2} \ln d + 59.950 + \ln(1 - e^{-.02996d})$ $- \ln(1 + 3e^{-.6376d})$
$\text{H}_2 \rightleftharpoons 2\text{H}$	$\ln K_c = -d - \frac{1}{2} \ln d + 57.635 + \ln(1 - e^{-.1217d})$
$\text{D}_2 \rightleftharpoons 2\text{D}$	$\ln K_c = -d - \frac{1}{2} \ln d + 57.892 + \ln(1 - e^{-.08488d})$

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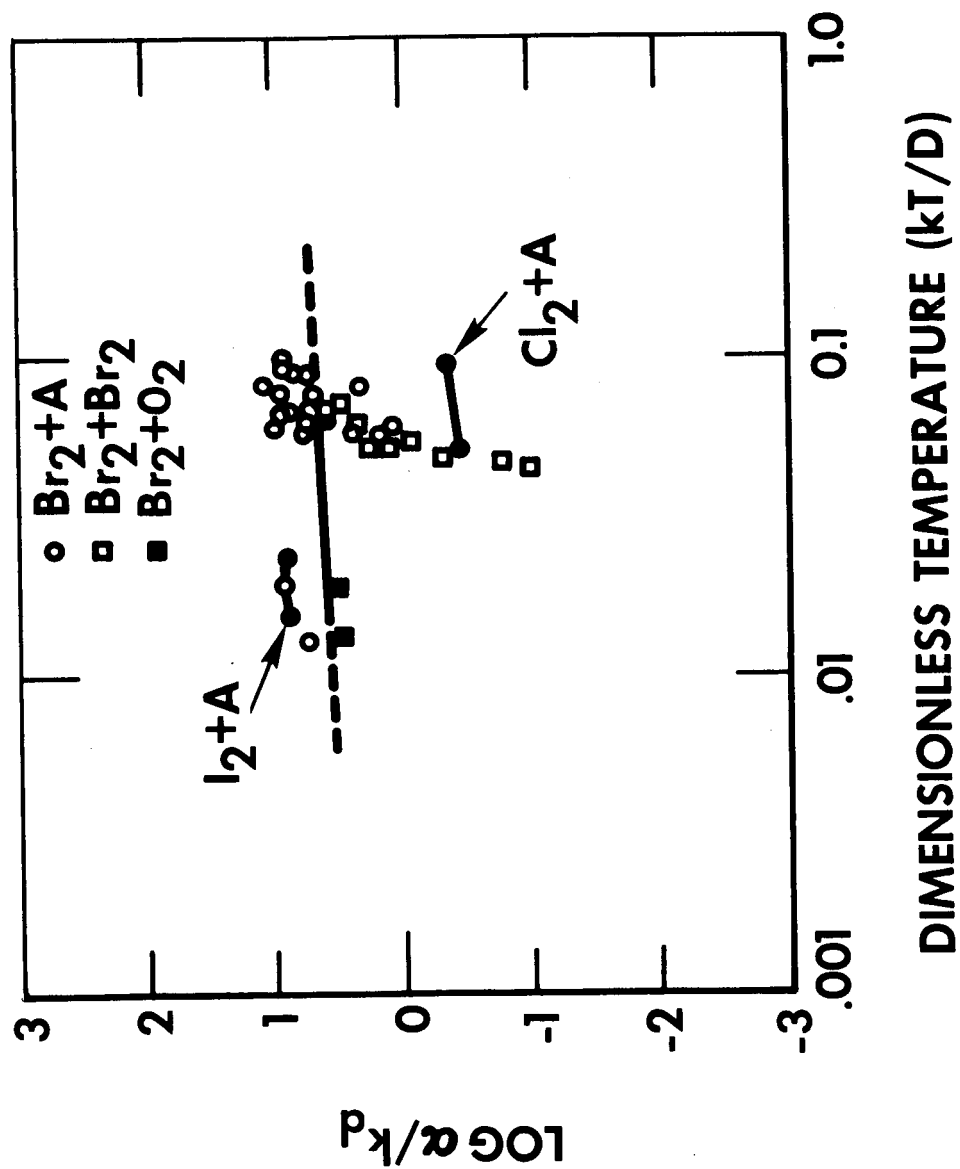


Figure 1 Dissociation of Halogens

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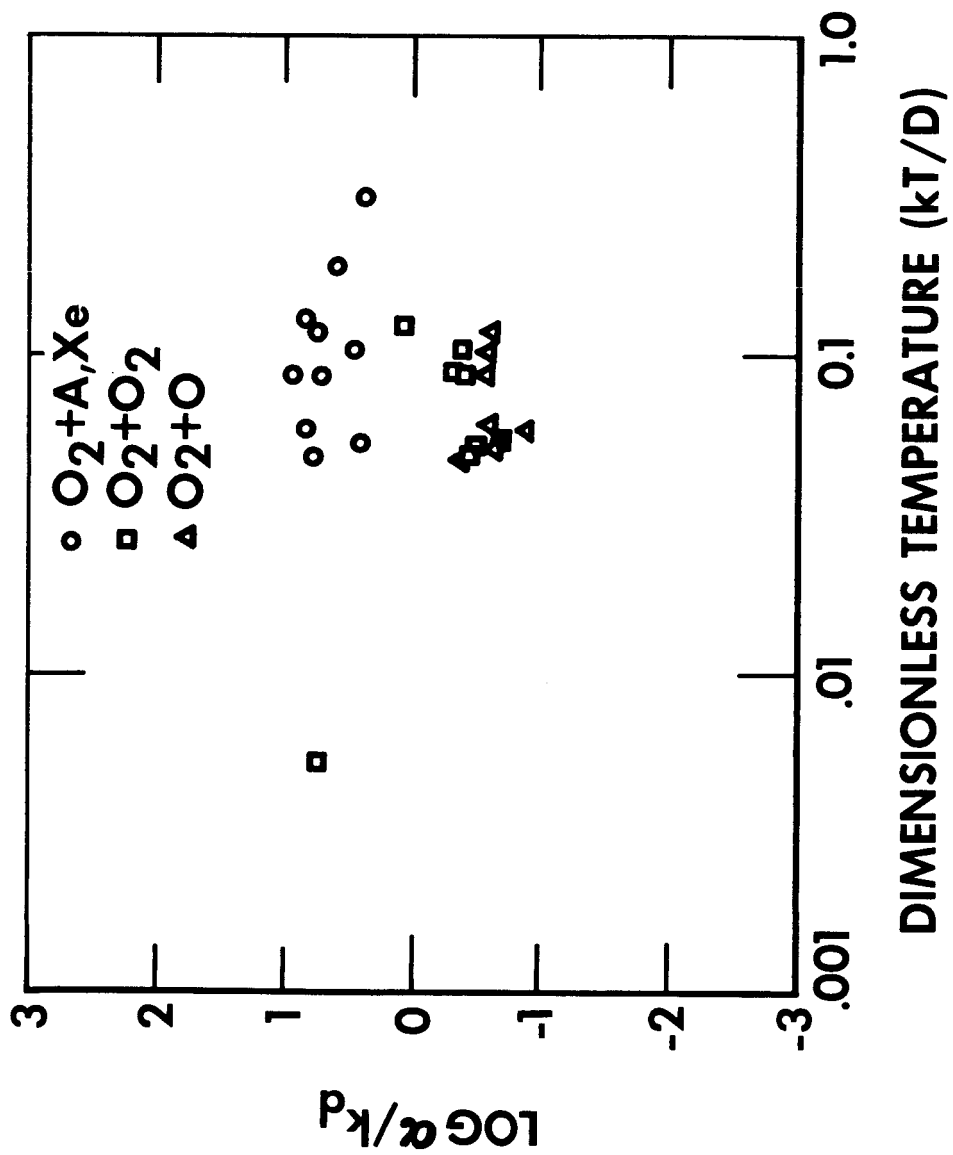
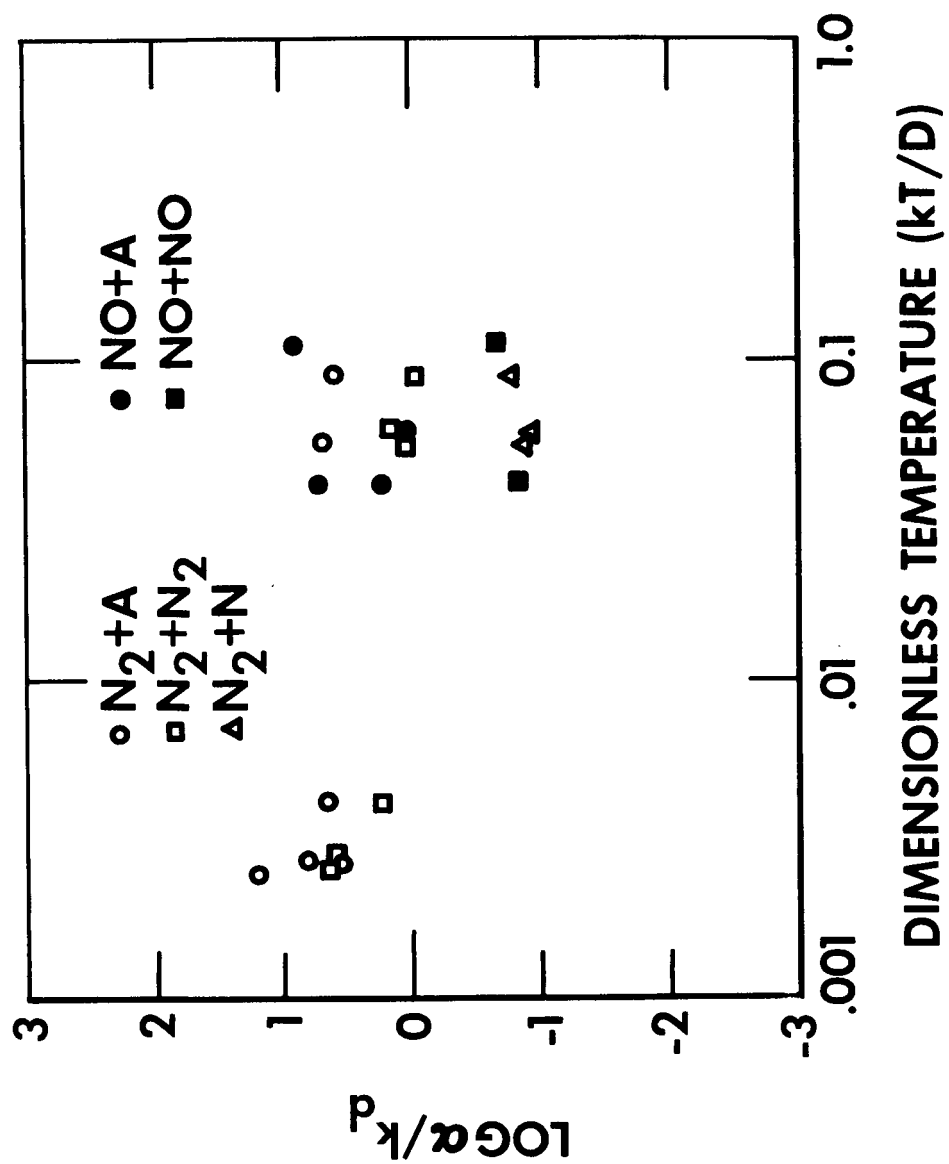
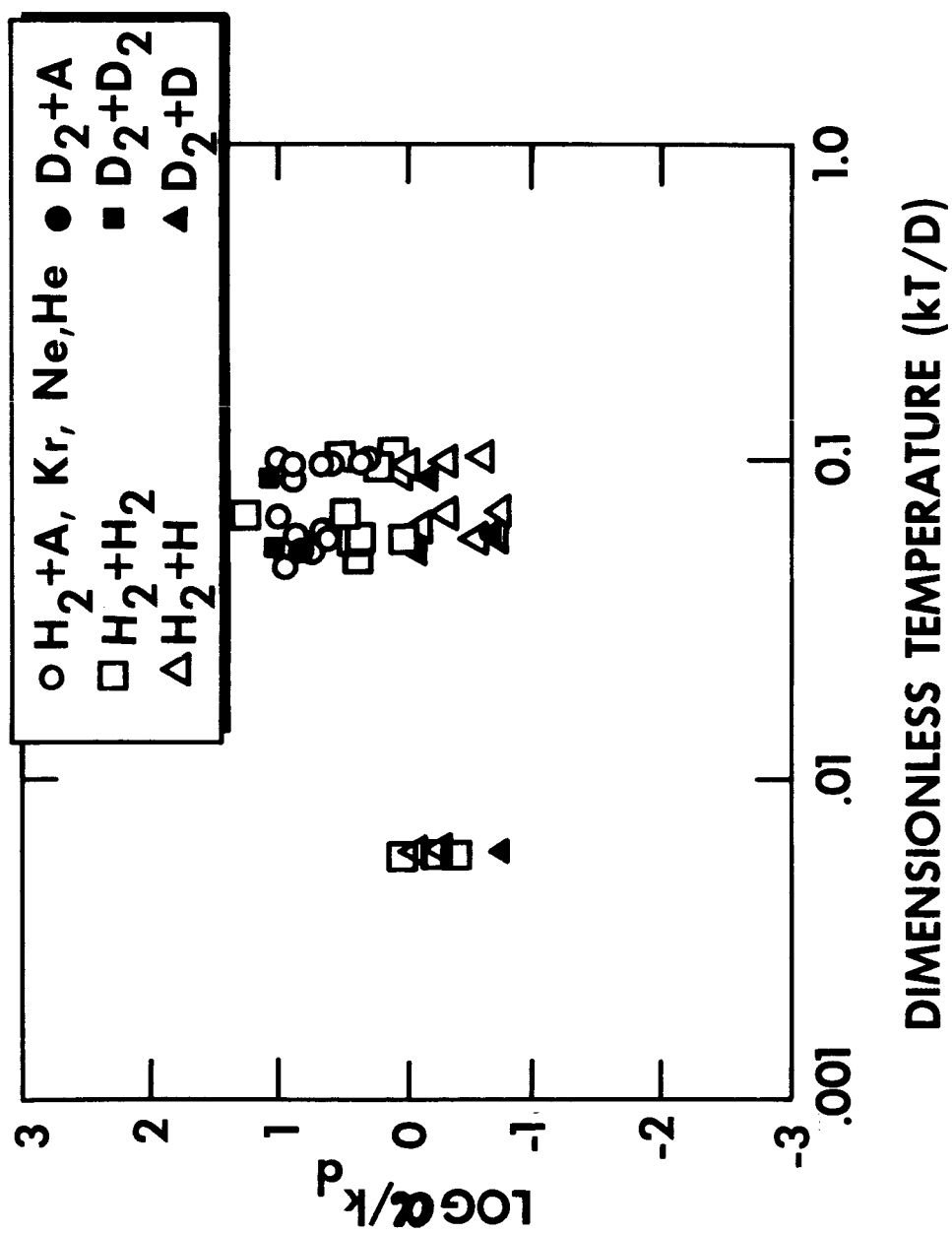


Figure 2 Dissociation of Oxygen

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Figure 3 Dissociation of N_2 and NO

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Figure 4 Dissociation of H_2 and D_2

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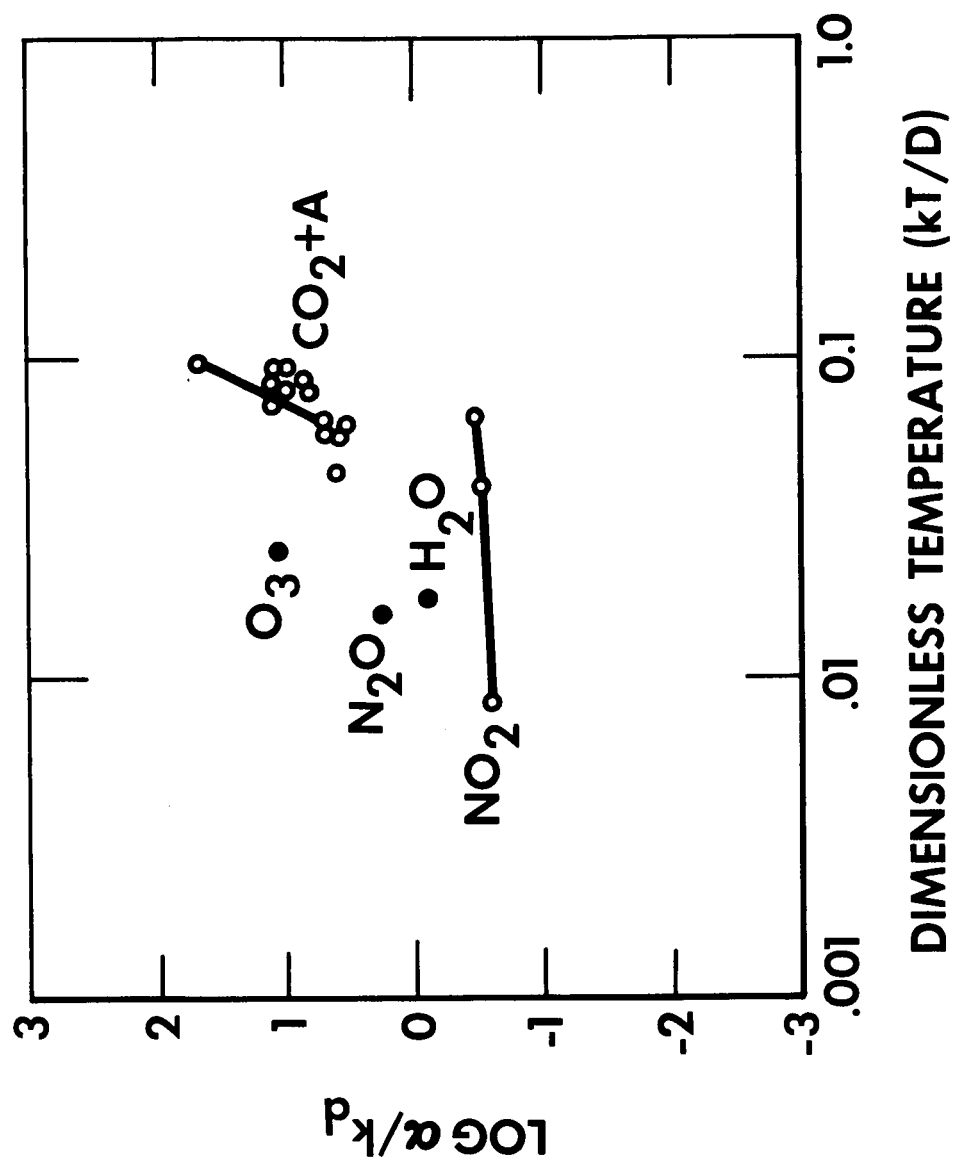


Figure 5 Dissociation of Triatomic Molecules